MULTI-SCALE REINFORCED

CARBON FIBER NANOCOMPOSITES

A Senior Scholars Thesis

by

AINSLEY VANROOYEN

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2008

Major: Aerospace Engineering

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Approved by:

Research Advisor: Zoubeida Ounaies
Associate Dean for Undergraduate Research: Robert C. Webb

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ABSTRACT

Multi-Scale Reinforced Carbon Fiber Nanocomposites (April 2008)

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Carbon fiber polymer composites are utilized in many industries including in commercial and military aircraft and space vehicles because of their lighter weight and superior strength compared to aluminum and steel. Due to the insulating nature of epoxy-based polymer composites and the dielectric breakdown of the epoxy, catastrophic failure may occur when subjected to high voltages (as in a lightning strike). The addition of carbon nanofibers and carbon nanotubes to the epoxy resin has the potential to improve electrical deficiencies and enhance mechanical characteristics, as well as add self-sensing and actuation capabilities to the original composite.

The focus of the present research is to modify the epoxy in traditional carbon fiber composites through addition of carbon nanofibers. As a first step, this study aims to develop an effective technique to disperse carbon nanofibers in the epoxy using mechanical stirring along with sonication, and characterize cured composite samples of various nanomaterial concentrations by optical microscopy, and mechanical and electrical characterization. Once the dispersion procedure is finalized, the nanofibers must be aligned in a desired direction to maximize the extent to which they enhance the original composite. This is achieved by placing electrodes on opposite sides of the material to apply an electric field while the epoxy cures, as secondary bonding joins the aligned nanofibers together. The Vacuum Assisted Resin Transfer Molding (VARTM)

process is currently used in industry and serves as a basis to add the modified epoxy resin to the carbon fiber fabric. Results will be tested and compared to a standard carbon fiber composite to optimize the overall procedure. With greater understanding and control of nanoparticles, it will be possible to design composites for specific applications in the not-so-distant future.

DEDICATION

I dedicate this work to my family, for the unconditional love and support they provide me in every aspect of my life.

ACKNOWLEDGMENTS

I would like to acknowledge my advisor, Dr. Zoubeida Ounaies, for her outstanding support and guidance along this journey. Her patience, flexibility and cheerful attitude bring much joy into the workplace. I must recognize my graduate advisor, Sumanth Banda, for his gracious teachings, advice, and his unending desire to lend a helping hand. My thanks go out to my friends at the Electroactive Materials Characterization Laboratory for all their help and support along the way. This work is supported in part by Dr. Lee and the Air Force Office of Scientific Research (AFOSR).

NOMENCLATURE

σ'	Conductivity
ε_o	Dielectric constant of vacuum
ε'	Dielectric constant
AC	Alternating current
AIBN	2,2'-azobis (isobutyronitrile)
CNF(s)	Carbon nanofiber(s)
CNT(s)	Carbon nanotube(s)
CO_2	Carbon dioxide
DMac	Dimethylacetamide
MnO_2	Magnesium oxide
PS	Polystyrene

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CHAPTER I

INTRODUCTION

This section covers background information on carbon nanomaterials and the benefits of their utility. Common difficulties in nanomaterial integration are discussed as well as the current methods used to solve these problems.

Carbon structures

Graphene sheets are sp^2-bonded carbon atoms that form a hexagonal plane template, which can be imagined to extend in all directions [1]. The single- and double-covalent bonding between carbon atoms gives high strength in the bonding direction, which in the case of a graphene sheet, is in its precise plane of existence. These sheets may be stacked to make graphite, whose loose, inter-laminar van der Waals attractions make the material highly susceptible to shearing. The rolling of a single sheet of graphene into a cylinder with sides covalently bonding together and ends capping with hemispherical buckyballs forms the simplest (single-walled) form of a carbon nanotube (CNT), depicted in Figure1(a). CNTs boast very high aspect ratios with diameters on the order of 1 nm and lengths extending to hundreds of micrometers [4], and exhibit excellent qualities in terms of stiffness, resilience, and mechanical, electrical and thermal characteristics.

This thesis follows the style of *The Journal of Composite Materials.*

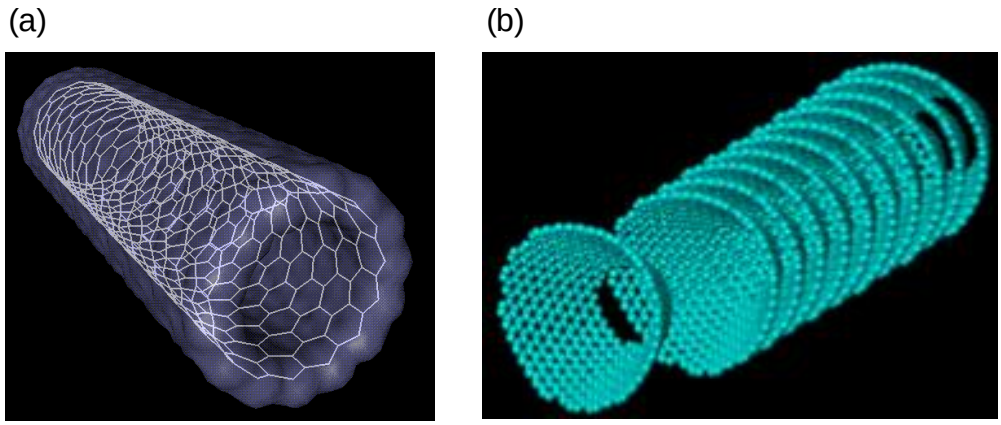


Figure 1. *CNT images of CNTs and CNFs. (a) Image of a single wall nanotube [2]. (b) Image of a carbon nanofiber [3].*

CNTs are prime constituents for advanced composite developments, vastly overshadowing the properties of its close cousin, the carbon nanofiber (CNF) of Figure 1(b). Despite its their many strengths, the difficulty in utilizing CNTs over CNFs is just as great. With a much higher surface area than CNFs, and thus greater Van der Waals attractions between elements, dispersion of CNTs within a solvent is quite troublesome.

Carbon nanofibers

Instead of a carbon-filled hexagonal web, CNFs are constructed from stacks of isolated, pentagonal-shaped carbon planes that are warped into cone-like structures [5]. As mentioned, advantages seen in CNFs are similar to those of CNTs, but are less pronounced; a low density adds little weight to the base composite, good electrical properties specifically address the task at hand, and a high aspect ratio with diameters ranging from 100 to 200 nm and length of 30 to 100 μm [4] give highly anisotropic behavior. CNFs are suitable for a wide range of applications from medical to consumer

products and industrial to high-tech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, energy storage, fuel cells, and information technology [5].

Dispersion of CNF

Naturally existing as unorganized bundles due to intrinsic van der Waals attractions, CNFs are not a convenient addition. If these nanoparticles can be homogeneously dispersed in a medium, the properties of the combined material will develop uniformity and allow predictable results.

Chung [6] studied how nanostructured carbons (including CNT, CNF and carbon black) are suitable for electromagnetic, electrochemical and thermal applications, such as shielding, battery electrodes and thermal pastes for microelectronic cooling. A method of dispersing the nanofibers in, in this case, a thermoplastic matrix, involves dispersing the nanofiber in an alcohol aqueous solution with the help of a trace amount of a dispersant. At room temperature, thermoplastic powder is added to the mixture with a blender such that the aqueous solution's alcohol concentration adjusts to allow thermoplastic particle suspension in the solution. The solution is then drained, dried at 120°C, and hot pressed uniaxially above the glass transition temperature of the thermoplastic at 1000 psi (6.9 MPa) for one half hour. Chung found that nanostructured carbon in the form of carbon nanofiber (0.1 μm diameter) is valuable as a filler in polymer-matrix composites for electromagnetic interference shielding after having been electroplated with nickel to

form a nickel nanofiber of diameter 0.4 μm, but it is not attractive as an additive in a polymer for attaining a composite of low electrical resistivity. The work also concludes that CNF is valuable for use as a porous electrode and as an electrically conductive additive in a non-conductive (MnO_2) electrode.

A common procedure in CNF dispersion in a solvent is the use of ultrasonication. Shen and Lee [7] worked with polystyrene (PS) /CNF nanocomposites to attempt to create mechanically enhanced polymeric foams of relatively small average cell size and high cell density. These composites were synthesized by adding different amounts of CNF to the styrene monomer, together with 2,2'-azobis (isobutyronitrile) (AIBN) as the initiator. The mixtures was then homogenized for 3 minutes and sonicated for 30 minutes, polymerized isothermally at 60 ºC for 20 hours, and post-cured at 105 ºC for 2 hours. The resulting foams (created with supercritical CO_2 as the foaming agent) were larger and less dense than desired due to low initial system viscosity, unable to prevent agglomeration of the CNFs. By adding 10 wt% PS into the polymerization system and increasing AIBN initiator concentration from 0.5 wt% to 0.75 wt%, foam density and system viscosity adjusted to the preferred levels.

Alignment of CNF

Due to its discontinuous nature, CNFs are far less effective than continuous carbon fibers when used as the sole reinforcement in composites [6]. If the CNFs were single, long strands that could be physically placed in a matrix where needed, there would be

one less issue involved in experiencing its value. With alignment, CNF fragments are able to line up and drift together by van der Waals forces to bond and create a virtually continuous chain; if the enveloping polymer is cured at this point, the CNF chain will be held in place and act like a single strand. The anisotropic trait of CNFs plays a major role when considering chain alignment. As long as the scientist can control the chosen method of alignment, the direction in which material properties become enhanced, deteriorated, or remain unchanged can be mandated to best fit the nanocomposite's intended application.

Electric fields have been utilized in the alignment of CNF, as in Lin's [8] exploration of aligned growth of CNFs/CNTs with variable orientations. Plasma-enhanced chemical vapor deposition (PECVD) was used, as it allows aligned nanoparticle growth on a substrate within a sheath. The final direction of alignment comes down to a matter of relative dimension between sample and sheath size; with a sample dimension much larger than the sheath region, CNFs/CNTs align perpendicular to the local substrate. When taking samples that lie completely within the sheath, nanoparticles align in the direction of electric field. In this case tilting the substrate imposes an angled nanoparticle growth direction with respect to the substrate normal.

Carbon fiber CNF polymer multiscale composites

More success has been found in hybrid composites involving both carbon nanofiber and conventional carbon fiber than in composites involving carbon nanofiber only [6]. The

CNF can be thought of as an enhancement to an already high-level product while the carbon fiber serves as the material backbone.

Nanofibers' high aspect ratio in alignment yields a new hybrid composite portraying anisotropic properties that can be assessed and taken advantage of. Because of their piezoelectric attribute, the materials under study are deemed "active" and react to stimuli of physical contact and electrical input. Resulting feedback comes in the form of electric signal production and actuation, and responses can be analyzed to learn more about the source acting on the material. Since the effectiveness of stimulus conversion to response as well as all aforementioned properties depend on the configuration of the composite at the nano-scale, it is critical to be able to understand and predict how the material behaves with changes in composition. Additionally, a good interfacial matrix-to-nanofiber bonding is difficult to achieve because of CNFs' atomically smooth, nonreactive surface [7]—a poor interface yields insufficient transfer of CNF properties.

Problem summary

As previously stated, the use of insulating carbon fiber polymer composites poses great danger to aircraft traveling through thunderstorms, as the electricity delivered by a lightning bolt would be confined to its strike location and cause material failure. With aligned CNF chains present, the resulting conductive material will dissipate the charge along paths of least resistance, and the relatively minimal damage can be easily located by visual inspection and repaired.

The addition and alignment of CNFs in the epoxy resin not only brings electrical enhancement, but also has the potential to create an improved multifunctional material in terms of sensing, actuation and increased strength. In order to fully extract these abilities, CNFs must first reach a homogeneous dispersion in epoxy solution. Van der Waals attractions between individual CNFs naturally cause agglomeration and the formation of bundles, significantly detracting from the true benefits to be had. The task of aligning CNFs in a common direction must then be met to provide paths of relatively low resistance for electric charge to travel and dissipate along.

The properties of a nanofiber-reinforced carbon fiber material are highly dependent upon the organization of nanofibers within the resin. For example, piezoresistivity varies with changing distances between adjacent nanofibers [9]. The effect is maximized if positioned with one-dimensional alignment, but van der Waals attraction, a high aspect ratio, and high surface area cause the nanofibers to naturally exist in clumps in the resin. The desired arrangement is realized through the use of electric fields, producing a transparent, homogenous resin solution, and adjusting concentrations gives even more spatial control to produce a preferable output.

This work focuses on integrating carbon fiber fabric with nanofiber-reinforced epoxy resin in order to address current electrical deficiencies in ordinary carbon fiber polymer composites. CNFs will be dispersed in a polymer matrix by sonication and mechanical

stirring. With a new method based on the current standard in composite-manufacturing, Vacuum Assisted Resin Transfer Molding (VARTM), new multiscale composites will be made with simultaneous polymerization and CNF alignment by electric field application.

Organization of chapters

This study consists of four chapters. Chapter I gives background on carbon nanofiber properties, applications, and the dispersion and alignment techniques that prepare them for utilization. Chapter II covers experimental procedures for dispersion of CNF inclusions in epoxy, aligning them by alternating current (AC) electric field during thermal polymer curing, as well as analysis by optical microscopy (OM) and electrical characterization. Chapter III lays out the results obtained from nanocomposite analysis and characterization, and Chapter IV concludes the work, offering insight for future advancement of this study.

CHAPTER II

METHOD

This section covers the manufacturing of carbon fiber epoxy composites, the processing and analysis of CNF and epoxy mixtures, as well as carbon fiber, CNF and epoxy three phase multi-scale composites. The CNF and epoxy mixtures can be made with two different methods which are explained in further detail. Preliminary in-situ alignment of CNF in epoxy, final CNF alignment during curing of epoxy, and post-processing electrical characterization methods are discussed as well.

Fabrication of carbon fiber polymer composites

Five-inch square panels of carbon fiber polymer composites are made from CRG Composite Kits, with the carbon fiber supplied by Airtech Advanced Materials Group. The original kit process is modified to accommodate the need to align CNFs through the panel's thickness. The final process, called the "hand lay-up" method, is shown in Figure 2. As shown, the carbon fabric is laid within a vacuum tape perimeter on an aluminum base. The fabric is covered with epoxy, flipped over and covered again, and a bleeder fabric is placed on top to absorb excess resin. An aluminum screen is used as the next layer, and another piece folded over the upper aluminum plate serves as a handle to help with removal after curing. A vacuum bag completely encloses the setup, connecting with the sealing tape. With the valve assembly, the vacuum pump is attached to pull out excess air bubbles from the sample, with the screens facilitating bubble movement up

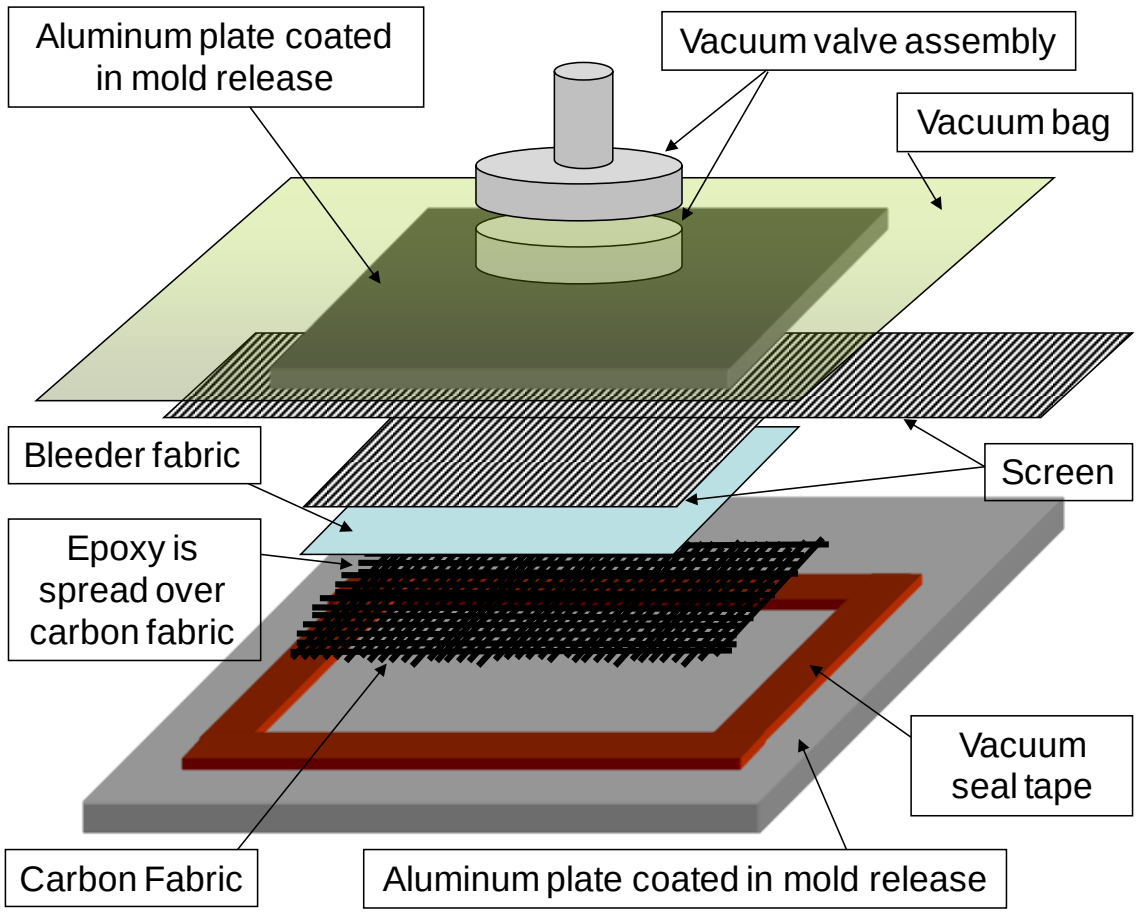


Figure 2. *Schematic of hand lay-up method used for fabricating carbon fiber polymer composites.*

and around the plate. The entire setup is then cured in a Sun System EC10A environmental chamber, with a LabVIEW program linked up with the appropriate curing schedule. Later, when a CNF and epoxy solution is used as the resin and alignment of CNF through the panel's thickness is desired, wires must be fed from voltage source to aluminum plates. Simultaneous alignment and curing follows a procedure explained in a following section.

CNF dispersion in epoxy

Purified CNFs are obtained from Applied Science Inc. and exist as clumps of strands joined by relatively strong van der Waals bonding. There are two methods utilized to break up these bundles and reach their homogenous dispersion in epoxy, but an initial step common to both procedures makes a notable difference; an amount of CNFs necessary to produce 0.1 wt% CNF in epoxy solutions must first be crushed using a mortar and pestle. The CNF is then ready for further processing.

Method A

The first method of dispersion aims to directly disperse the CNF in a catalyst, or hardener. The particular epoxy-hardener pair is EPON 862 and Epicure 3282 from Miller-Stephenson Chemical Co., with a mixing ratio of 100 : 26.4 and a curing schedule of 2 hours at 121^{o}C and 2 hours at 177^{o}C. Unless noted, all calculations to follow are consistent with producing a 10g solution of 0.1 wt% CNF in epoxy. The desired hardener amount is measured in a 100ml flask. The prepared CNF is carefully added and readied for mechanical stirring and sonication. An Ika RW 20 Digital mechanical stirrer holds the stirring setup vertical, which consists of a glass rod and glass shaft. Grease helps the two pieces resist slipping. The glass rod-and-shaft connection fits with the flask shaft adding stability and preventing additives in the air from entering. The rod is rotated by the stirring motor at approximately 150 rpm, and an attachment at the rod's opposite end mixes the fluid. For sonication, a Cole-Parmer Ultrasonic Cleaner is used. The flask is placed such that the bath water line is above the flask content mixture line to

ensure effective sonication. Ultrasonic waves in the bath disturb the secondary bonds within CNF clumps to disperse the individual strands. An optimal stirring time must be found that achieves a desired degree of dispersion before negative returns appear from over-sonication, like the possibility of CNF strand breakdown as well as solution temperature increases, which may begin curing to some degree in later steps. The target time for this step is found to be 4 hours. Next, stirring is halted and the rod is removed so epoxy can be added from a beaker. This is carefully done, as intermediate mass scale measurements of the beaker are required to track how much epoxy is entering the system. The particular scale used is a Mettler Toledo B204-S. After this addition, the mixture is stirred and sonicated for another 3 hours. Although this particular epoxy undergoes little curing at room temperature, the temperature increase in this stage of mixing is more important than before as this may somewhat speed the curing process. The chemical reactions from the formation of cross-link bonding in the epoxy release bubbles into the mixture throughout this stage. After this second sonication, a Fisher Scientific Isotemp Vacuum Oven Model 280A is elevated to 60^{o}C to reduce the viscosity of the mixture. This allows a Fisher Scientific Maxima C Plus vacuum pump easier removal of the air bubbles from the liquid, leaving the final result.

Method B

The main difference in this alternate method is the initial dispersion of CNF in dimethylacetamide (DMac) instead of the hardener, because of its proven success in dispersion of CNTs [10]. An appropriate amount of DMac for this sample size is

approximately 5g, which is measured into a 100ml flask. The prepared CNF is added and the mixture is similarly stirred for 3 hours. As per Method A, the epoxy is added and sonication repeats for 3 additional hours. Removal of DMac from the mixture is needed for a purely CNF and epoxy mixture. To reach this, the flask is placed in the vacuum oven at 90 ^{o}C to fully evaporate the DMac. The pump pulls out gaseous DMac, taking a night to reach completion. To verify DMac removal, flask weights before and after evaporation are compared. The final steps are to add the required hardener amount and remove bubbles by de-gassing in the vacuum chamber. So that the two methods are comparable, Total sonication time is set to 7 hours for both CNF dispersion methods so the results are comparable.

Optical microscopy of CNF and epoxy solution

For each step of solution processing it is possible to monitor CNF dispersion progress by way of transmission optical microscopy. A Carl Zeiss Axiovert 200 is used for this characterization. Mechanical stirring and sonication may be paused at any point during either method to take solution samples on a glass slide. These samples are then viewed at 10x, 20x, and 50x magnifications to draw conclusions on the effectiveness of the dispersion.

In-situ alignment of CNF in epoxy mixture

Once dispersion of CNF in epoxy is completed, the focus shifts to CNF alignment in a desired direction within the epoxy matrix. The high temperatures needed to cure the

epoxy make it difficult to observe alignment of CNF during a high temperature cure. By testing alignment in-situ and at room temperature, deductions about alignment behavior under the real conditions can be made before proceeding. The optical microscope gives images of CNF alignment over time at 10x, 20x, and 50x magnifications, with overall testing procedure seen in Figure 3. Two 2mm x 4.5mm x 4mm copper bars are super-glued 1cm apart onto a glass slide and a wire is soldered to each. An Agilent 33220a 20MHz Function/ Arbitrary Waveform Generator supplies voltage to a TREK Model 609E-6 High Voltage Amplifier, and by connecting positive and ground leads to the copper electrodes, an electric field of 100 V/mm is achieved with the flip of a switch. Choosing an AC voltage source adds frequency variation to alignment, and once understood this feature becomes a control. The 10 Hz, 1 kHz and 10 kHz are the subject

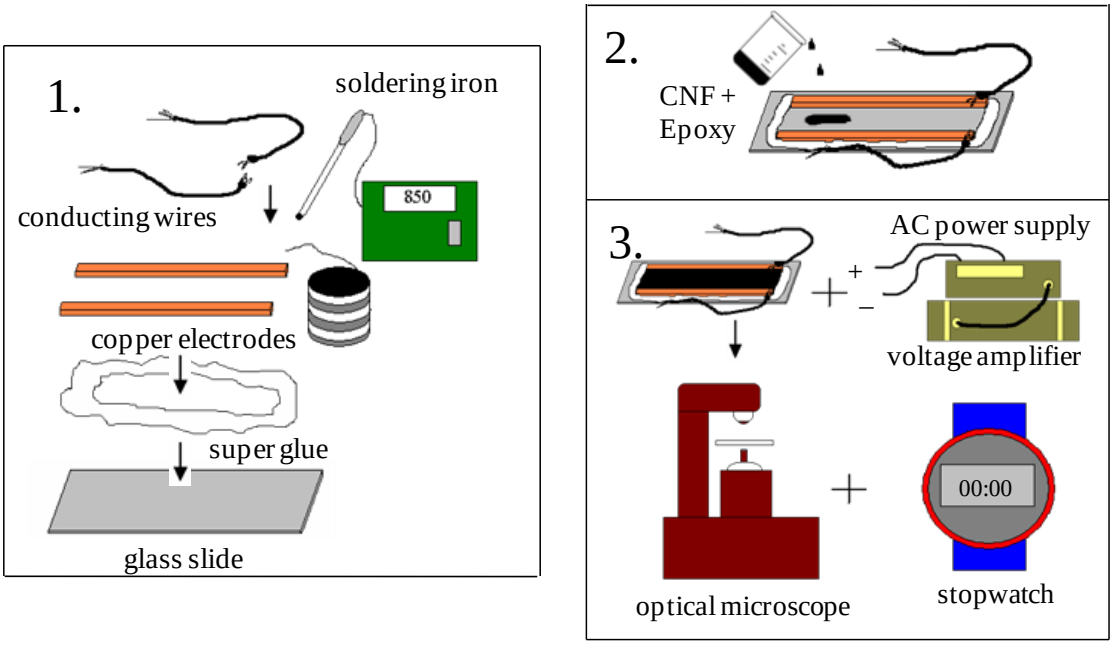


Figure 3. *In-situ CNF alignment test schematic.*

frequencies of this analysis. A small amount of 0.1 wt% CNF in epoxy is placed between the electrodes, and the slide is placed on the microscope for testing. From the time of electric field application, optical microscopy images are captured at minutes numbered 1, 3, 5, 10, 20, and at each 20- or 30-minute total time increment following. At 90-120 minutes the electric field is removed and images are taken for another 5 minutes. There are several factors to consider in the overall process: CNF initial time response to the applied electric field, the rate of chain formation, the average thickness of CNF chains and their average spacing, and CNF behavior after removal of the electric field.

Simultaneous alignment and curing of CNF in epoxy mixture

This process is similar to the in-situ alignment phase but introduces thermal effects from curing of the epoxy, resulting in CNF chain structures inside a hardened epoxy matrix. Instead of a glass slide, the solution rests in a silicone mold made from HobbyMold 160. This mold is ideal for work with epoxy because of its natural release from epoxy's strong adhesive effects. The mold is made so that similar copper electrodes can be inserted and held in place, and used as before with wires connected on their tops. When the solution is added between the electrodes, it will fill a 4mm x 15mm x 30mm volume, with the electrodes placed as shown in Figure 4. The environmental chamber is used to create a high temperature environment for curing. The same voltage input setup is utilized, and the electric field is applied with the simultaneous start of the curing cycle. Wires connecting the voltage source to the copper electrodes are fed through an opening in the chamber. Coupled with LabVIEW, the chamber's temperature change rate can be

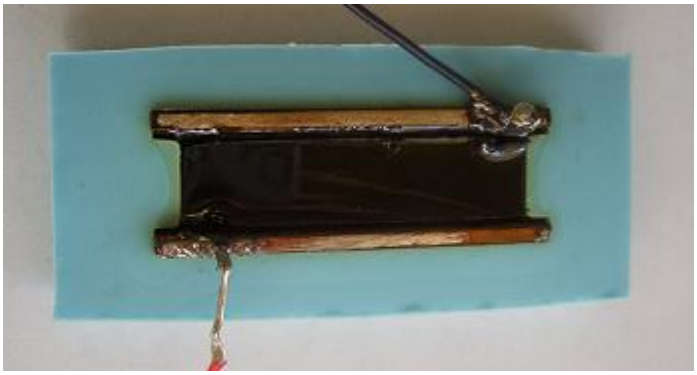


Figure 4. *CNF in epoxy aligned and cured in silicone mold between copper electrodes.*

set, as well as the soak times at desired temperatures. The rate of temperature change is set to 20 ^{o}C/min and the two soak times to 120 minutes. Starting the program immediately increases the chamber temperature from its current condition to target temperature number one, 121 ^{o}C for the first soak time, then 177 ^{o}C for the second. At completion, heating automatically ceases and the chamber cools naturally to room conditions.

The electric field must only be applied as long as needed to develop the CNF chain structure and maintain them. At a certain point during curing, the epoxy becomes viscous enough to inhibit chain deformation in the absence of electric field. This point is determined by a qualitative analysis of CNF and epoxy viscosity during a normal curing schedule. Possible high temperature effects on CNF dispersion in epoxy (i.e. clump reformation, clump movement) are studied as well by taking samples on a glass slide with the back end of a Q-tip and observing under the optical microscope. The samples are taken at 15-mintute intervals until the solution becomes too viscous.

Conductivity characterization and dielectric spectroscopy

Samples containing aligned CNF chains at different frequencies can now be characterized by viewing with optical microscopy and then property analysis. The electrical properties discovered can be compared to samples of pure epoxy as well as samples of random CNF dispersion to see if any beneficial results have been achieved with aligned CNFs.

A Novocontrol Broadband Dielectric Spectrometer is used to find the AC electrical conductivity of the aligned CNF in epoxy composites. Samples are first cut using a Struers Secotom-10 diamond blade saw and then polished with a Struers RotoPol-31 to a desired sample size of approximately 3mm x 8mm x 20mm. Opposing surfaces of a sample are painted with silver paint as required by the spectrometer and placed in the machine for measurement. By introducing alignment in the composites, inherent properties have now become anisotropic and conductance must be considered and tested in two different directions with respect to alignment direction. This is further described in Figure 5. In theory, conductivity should increase in the parallel direction as incoming current now has paths of CNF chains that allow passage through the material. Since there is no electric field set in perpendicular direction, there should be no CNF chains and no noticeable change in conductivity.

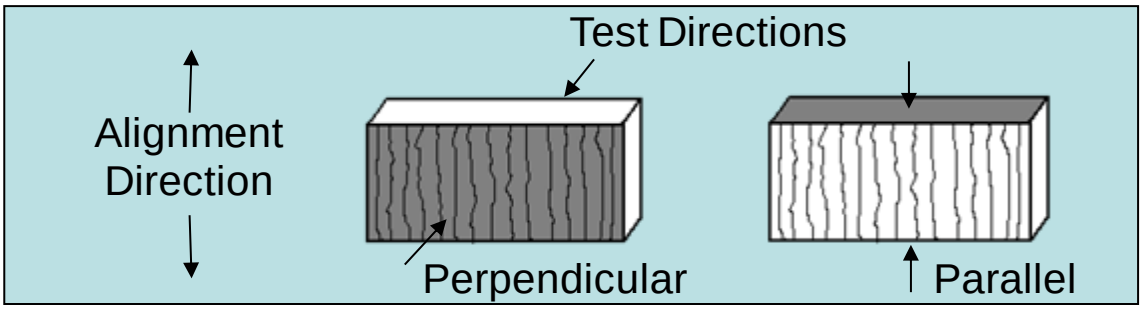


Figure 5. *Directional property testing with respect to CNF alignment. Opposing faces are painted with silver paint.*

The spectrometer applies voltage while varying frequency and the conductance is measured. This is then used to find the conductivity by the equation

$$\sigma' = \frac{g * t}{A} \tag{1}$$

Where σ’ is conductivity, g is conductance, t is sample thickness and A is sample area.

As with measuring conductivity, the dielectric constant is measured using the same setup. In addition, both properties are plotted simultaneously versus frequency during single test. The dielectric constant is used to tell of an insulator’s ability to store electric charge, with a relation shown by

$$\varepsilon' = \frac{C * t}{\varepsilon_0 * A} \tag{2}$$

where ε’ is the dielectric constant, C is the capacitance, t and A are thickness and area of the sample, and ε_0 is the dielectric constant in vacuum, equal to 8.885×10^{-12} F/m.

CHAPTER III

RESULTS

Fabrication of carbon fiber polymer composites

The original CRG composite kit uses epoxy that cures at room temperature, while EPON 862 requires much higher temperatures. The asymmetric weave of the carbon fiber causes an unbalanced contraction when cooling, resulting in panel bending as seen in Figure 6 (a). This effect is negated by using an additional layer of fabric and placing it mirror image to the original. The epoxy must be poured on all four faces of carbon fabric. Another important issue is the necessity of eliminating all voids in the panel, which are locations where there are air bubbles in the epoxy or where the epoxy did not fully wet the fabric. These voids act as strain concentrations and affect the overall effectiveness of the material. This problem arises from insufficient de-gassing of epoxy, as well as failure to create an air-tight vacuum seal for final gas removal in the hand lay-up method. Figure 6 (b) shows close-ups comparing a panel with high numbers of voids to one with no visible voids. After addressing these concerns and developing a working technique, the final result is a 5'' x 5'' panel, seen in Figure 6 (c). When ready, the procedure is configured to include wire leads and electric field application to align CNF through the panel thickness.

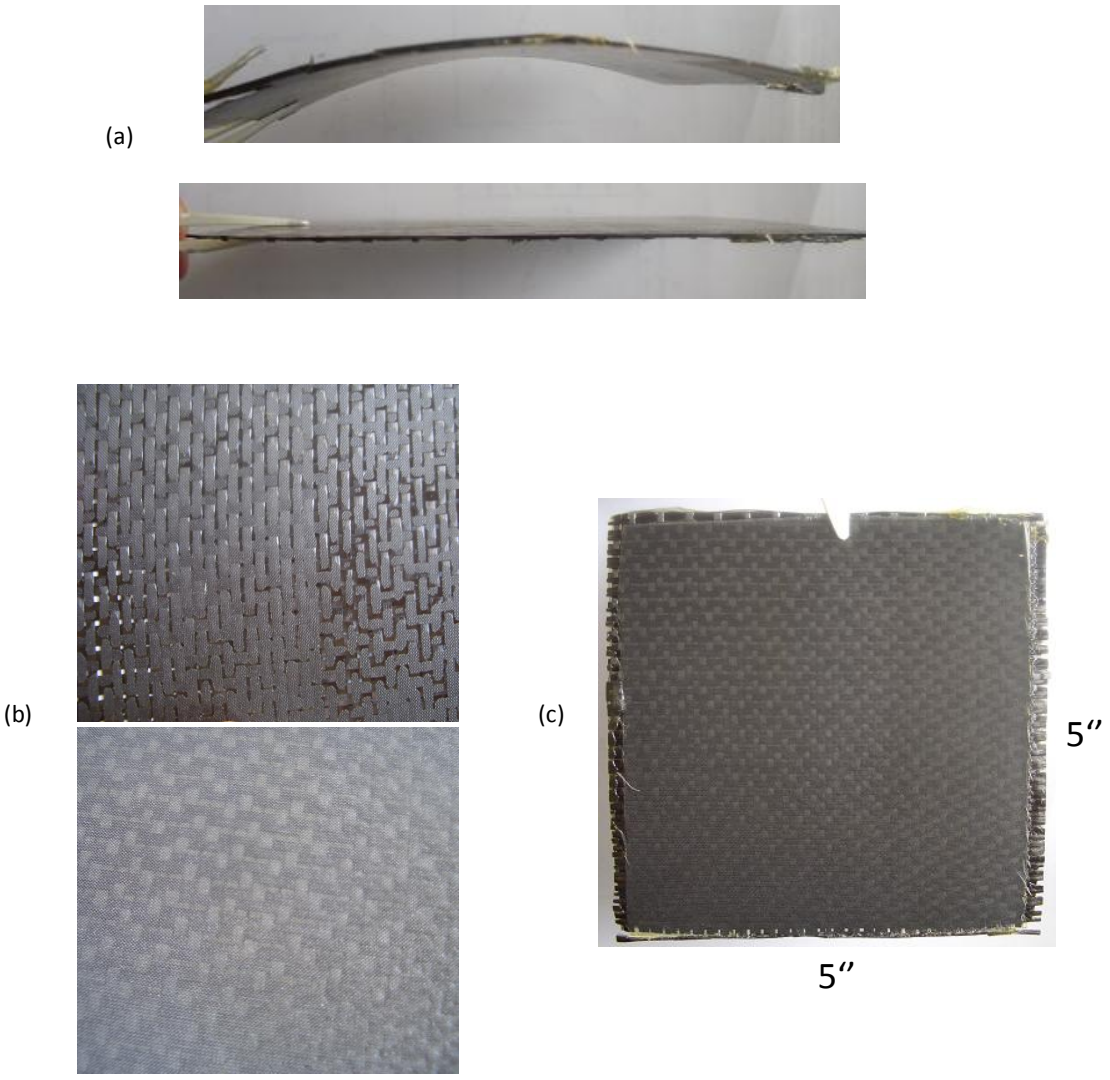


Figure 6. *Carbon fiber composite panels. (a) Image comparing a single-ply panel with bending from unequal contraction in cooling to a two-ply, panel with mirror image placement. (b) Image focusing on panel voids and comparing to one without. (c) Final result with proper technique.*

CNF dispersion in epoxy and solution characterization

Solutions of 0.1 wt% CNF in epoxy are made by Methods A and B and resulting solutions are investigated with optical microscopy. Initially, both methods would begin without crushing CNF by mortar and pestle, and would sonicate an hour less in the first

step of dispersal. By using the mortar and pestle and experimenting with sonication times, optimal conditions were found to include CNF crushing and the additional hour of sonication.

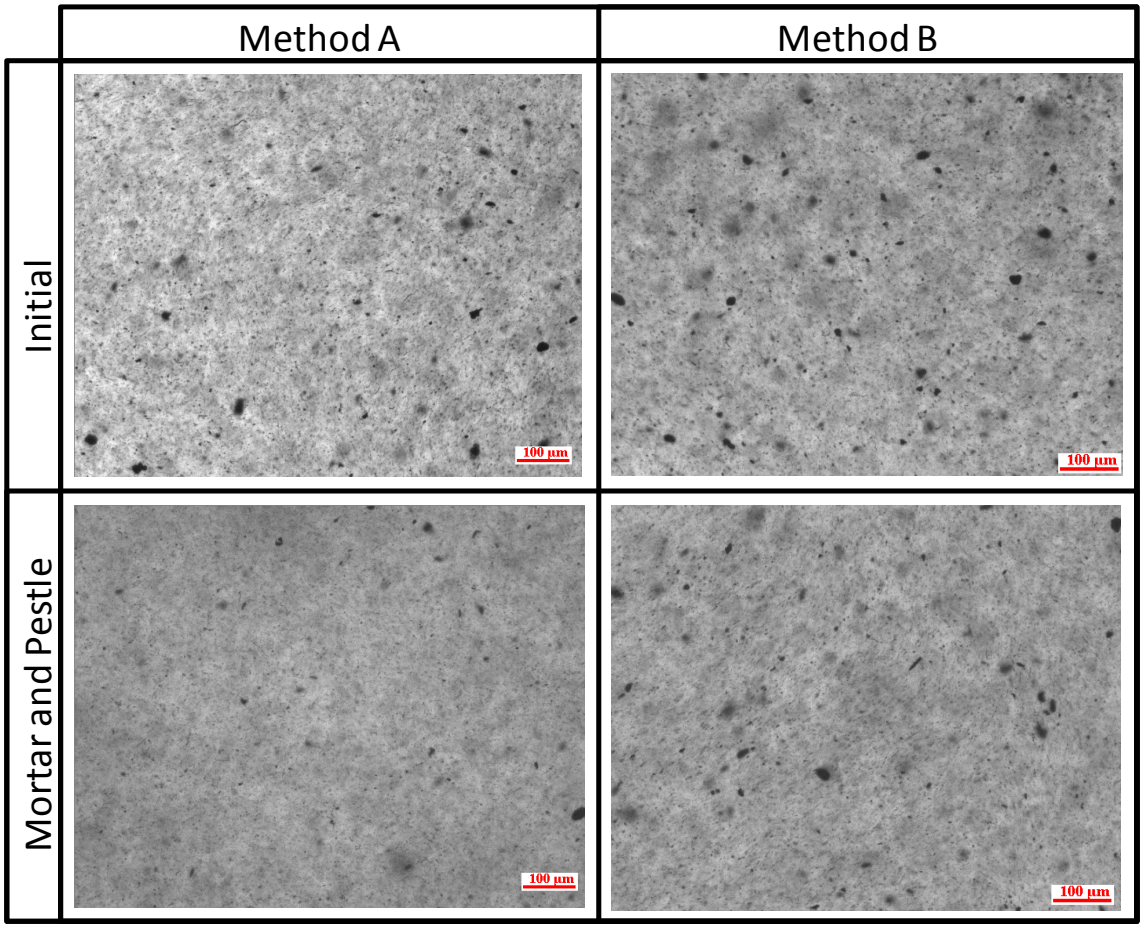


Figure 7. *Mortar and pestle effect on methods A and B CNF dispersion.*

Figure 7 shows both the frequency and size of CNF clumps in Method A to decrease a notable amount with the added changes. Method B improves as well, but not to the same

degree. At this point in the experimental process Method B with mortar and pestle had been subjected to several tests. This method is highly sufficient for the designed purpose, and is used for the remaining tests to maintain consistency.

In-situ alignment of CNF in epoxy mixture

CNF alignment and chain formation is monitored with in-situ alignment testing. An input voltage of 100 V/mm is used at frequencies of 10 Hz, 1 kHz and 10 kHz. Initial application of the electric field caused solution disturbance in just the 10 kHz frequency

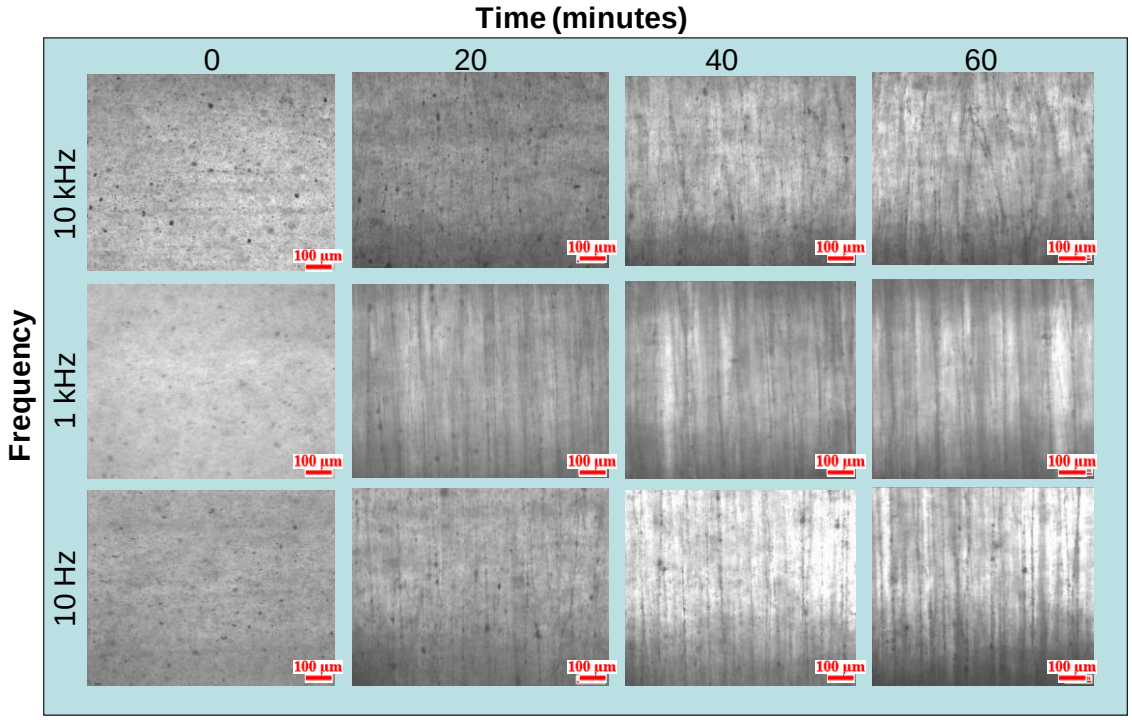


Figure 8. *In-situ alignment test results at three frequencies.*

case, causing the solution to move in various directions. Over time solutions form noticeable chains by the 20th minute under the electric field as seen in Figure 8. All three cases reach a more complete alignment over time, but results are not posted in shown figure past 60 minutes due to minimal activity. Additionally, the removal of the electric field requires a substantial amount of time, close to 10 minutes, to show any chain disturbances that will affect the overall product. The hardening of the epoxy under real conditions will also assist in chain maintenance and further decrease any worry over this issue.

Simultaneous alignment and curing of CNF in epoxy mixture

Epoxy viscosity change while curing was studied to find out exactly when it becomes stiff. At that time, the electric field must complete alignment of CNFs into chains, since further electric field application will no longer budge the fibers. The resulting empirical analysis is given in Figure 9. Figure 9 (a) shows the curing cycle of EPON 862 and times that samples were taken, Figure 9 (b) showing the corresponding empirical viscosity of the solution. As depicted, 90 minutes of simultaneous electric field application and curing time is enough to form the internal structure. All tests following are conducted by turning voltage source off after the first 90 minutes of application. It is also found that CNF dispersion is unaffected during cure.

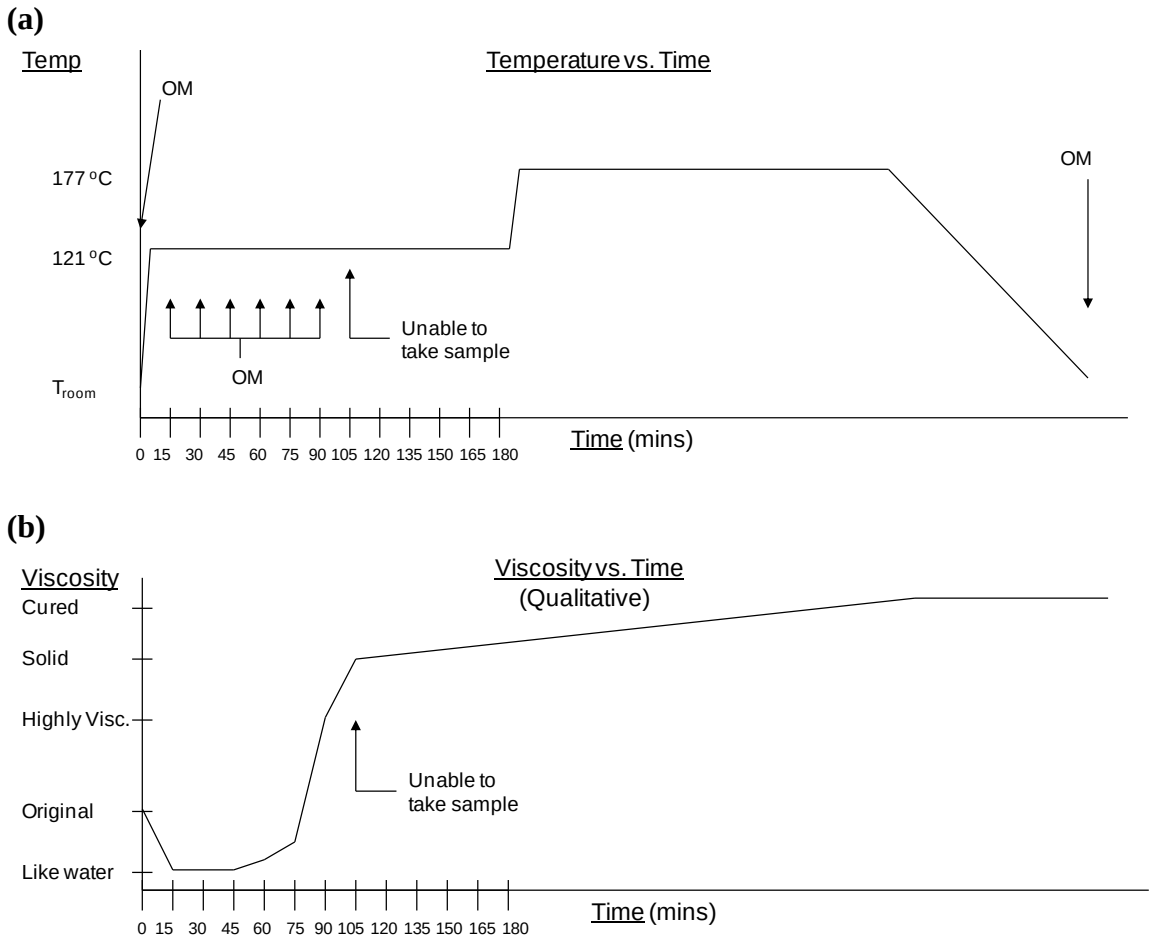


Figure 9. *Qualitative viscosity analysis of curing epoxy. (a) Curing schedule of EPON 862. Viscosity is monitored in 15-minute intervals until solidification. (b) Qualitative results of epoxy viscosity over time.*

Conductivity measurements of cured epoxy with aligned CNF

The conductivity of epoxy with aligned CNF chains using different AC frequencies is found in parallel and perpendicular directions relative to chain formation, as explained in Figure 5. Tests on pure epoxy as well as randomly-dispersed CNF in epoxy were conducted as a base reference for comparison. The tests are spilt and analyzed in the parallel and perpendicular alignment groups.

It is known that material conductivity (σ', in S/cm) is drastically different between conductors and insulators. In a plot of conductivity versus applied AC frequencies, the difference is seen as a greater, constant conductivity in conductors compared to a linear increase in conductivity with frequency for insulators. Figure 10 reports the conductivity of samples tested parallel to alignment direction. The pure epoxy shows a trend similar CNF into chains brings promising results. Aligning with low AC frequencies of 0.1 Hz to insulators, as expected, with an initial conductivity on the order of 10^{-15} S/cm. Adding

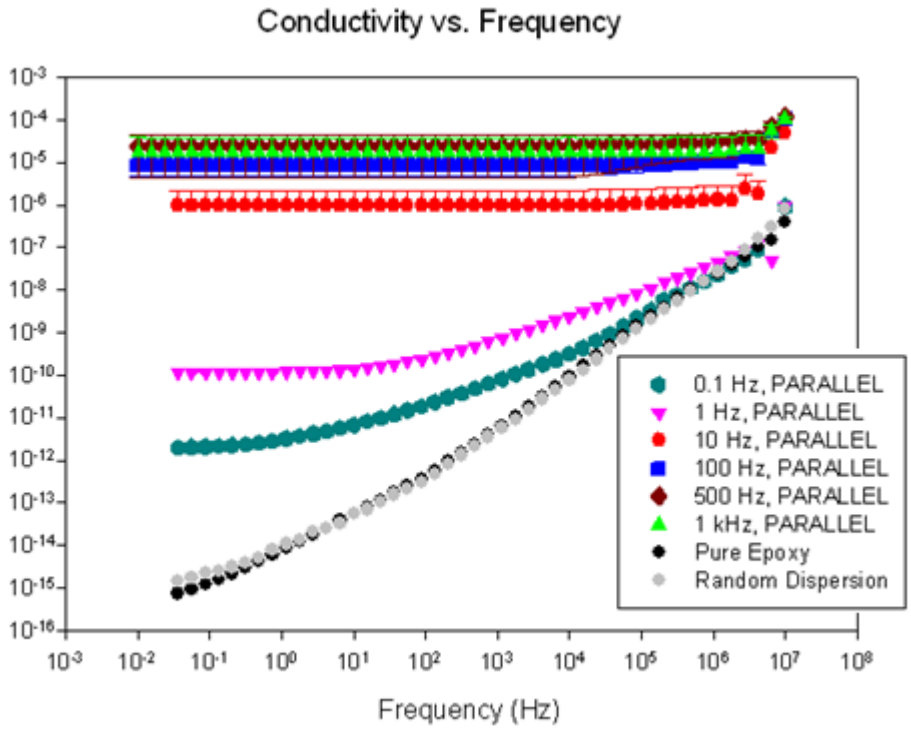


Figure 10. *Conductivity measurements parallel with CNF alignment.*

randomly dispersed CNF has no effect on conductivity, but the next step of aligning and 1 Hz give a noticeable increase in initial conductivity by 3-5 orders of magnitude. Frequencies of 10 Hz, 100 Hz, 500 Hz, and 1 kHz cause the material to behave purely as a conductor. Initial conductivity readings are 9-11 orders of magnitude greater than pure epoxy, and values remain constant despite changing frequency. When closely considered, the maximum conductivity belongs to the 500 Hz frequency, with a slight drop when moving up to 1 kHz.

Conductivity data is also gathered for the direction perpendicular to CNF alignment, seen in Figure 11. All but the 100 Hz and 500 Hz frequencies yield initial conductivities 2-4 orders of magnitude greater than the pure epoxy and randomly dispersed CNF sample value (close to 10^{-15} S/cm), and continue to increase like normal insulators. The most interesting cases are the three highest frequencies. The 100 Hz and 500 Hz frequencies have the largest conductivity jump of 8 orders of magnitude, and the 1 kHz frequency shows similar behavior as the lower frequencies. These results imply that a range of frequencies produce CNF chain formations that branch out in directions other than what is imposed by the electric field. These frequencies allow individual chains to intertwine in a way that some connection is established between faces considered in the perpendicular testing direction. The 1 kHz frequency does not portray this behavior and functions primarily as a very weak conductor at best. These results show the possibility of creating electrically isotropic nanocomposites as well as anisotropic materials, with conductive traits in a single, predetermined direction.

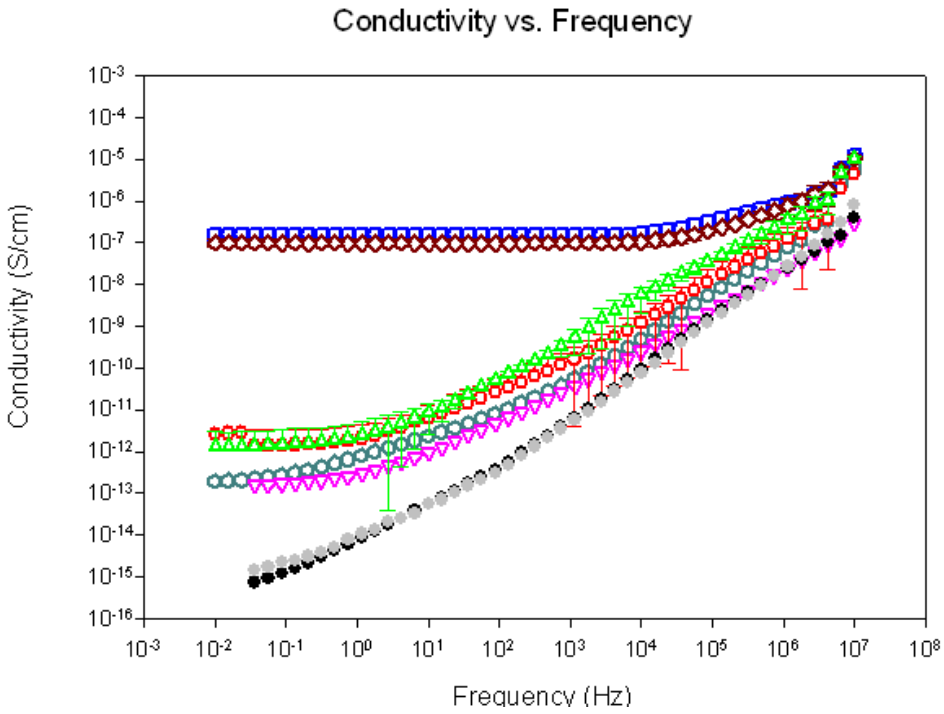
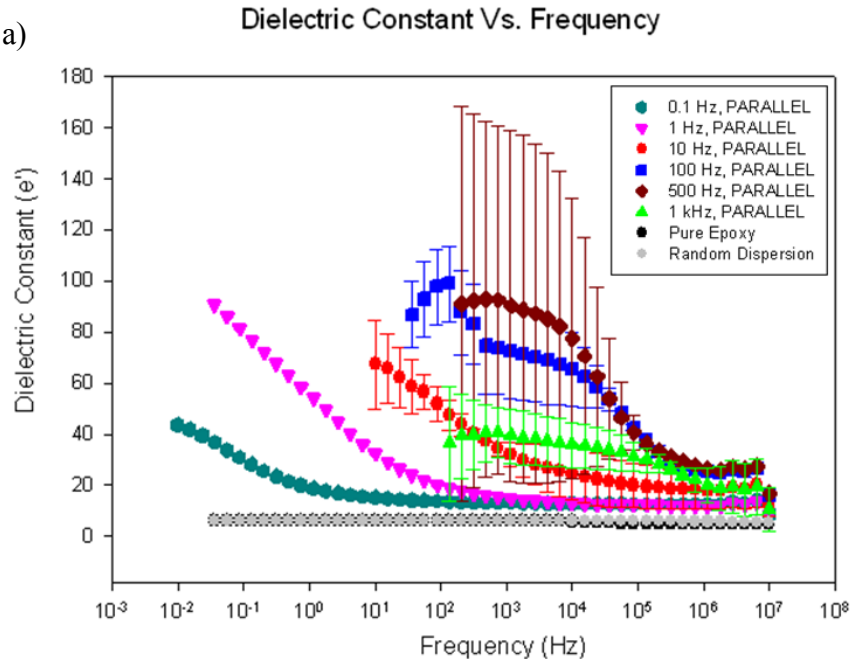


Figure 11. *Conductivity measurements perpendicular to CNF alignment.*

Dielectric constant of cured epoxy with aligned CNF

The dielectric constants for epoxies with aligned CNF chains using different input AC frequencies are found in parallel and perpendicular directions relative to chain formation. A characteristic of conductors is a decreasing dielectric constant with increasing frequency, while insulators maintain a low, constant value over the domain. As seen in Figure 12(a), the dielectric constants for samples in the direction of CNF alignment have significantly different values compared to the purely insulative epoxy. The 100 Hz and 500 Hz samples possess the greatest dielectric constant at the highest frequencies. In Figure 12(b), similar results are found in the perpendicular direction but

a)



b)

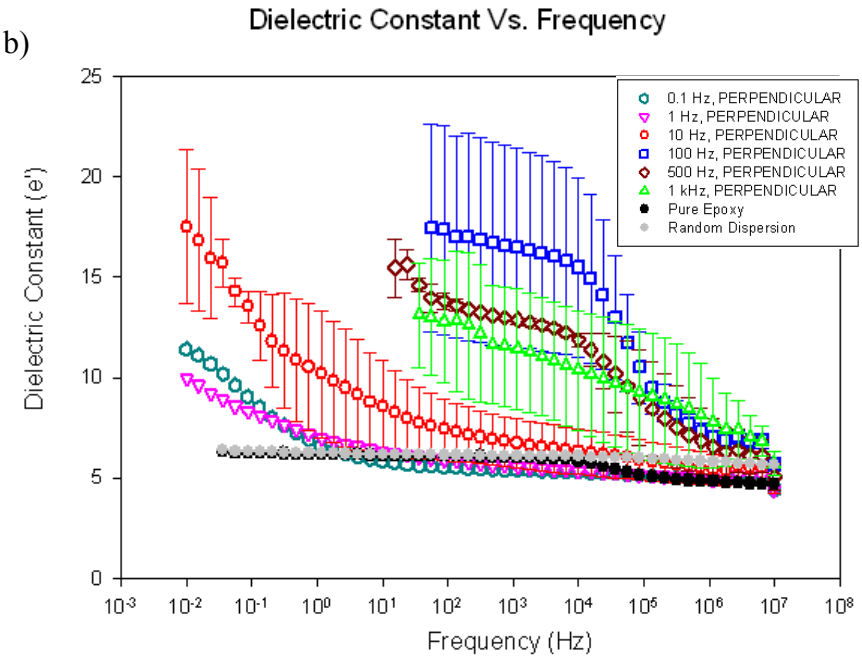


Figure 12. *Dielectric constant measurements in epoxy with CNF alignment. a) Dielectric constant measured parallel to CNF alignment direction. b) Dielectric constant measured perpendicular to CNF alignment direction*

at a smaller scale. The same decreasing dielectric constant behavior is shown but with lower magnitude.

Digital imaging and optical microscopy

The completed epoxy samples with CNFs aligned at various frequencies are imaged with a digital camera and by transmission optical microscopy. In this way, qualitative analysis of physical chain structure is obtained, which helps put reason to the properties discovered for each sample.

Figure 13 shows images that include chain formation at 10 Hz, 100 Hz, 500 Hz, and 1 kHz input frequencies. In all cases, CNF chains group together to form thicker columns. This allows visibility through the sample, showing many thinner chains evenly dispersed throughout the sample length. This overall behavior differs in the 1 kHz case with the absence of thin, completed chains in the sample. The thick chains of 1 kHz alignment are more defined, are kinked in some places and seem more tightly packed than, for example, the 10 Hz chains. The 100 Hz and 500 Hz samples show the groupings of chains to be consistently thick across the sample, leaving fewer gaps. The close interactions between these thick chains are what give the 100 Hz and 500 Hz greater conductivity ratings in the perpendicular direction compared to the 1 kHz case.

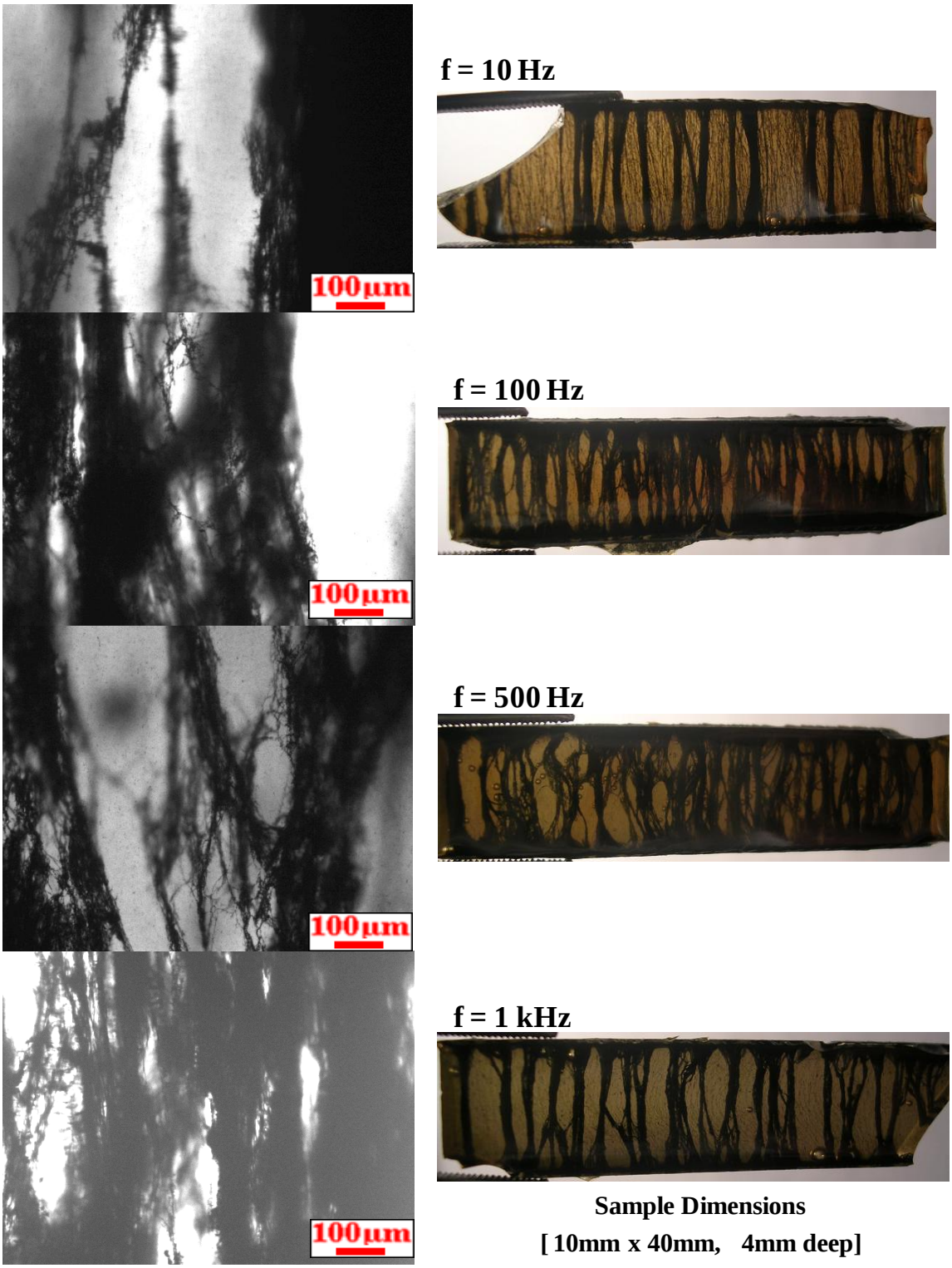


Figure 13. *Digital and optical microscopy of aligned CNF in epoxy samples.*

CHAPTER IV

CONCLUSIONS

The main goal of this study was to improve the conductivity of carbon fiber polymer composites by adding and aligning carbon nanofibers in the epoxy matrix. In pursuit of this ambition, composite panels have been made. CNFs were successfully and homogenously dispersed and aligned in epoxy, and the electrical properties were characterized.

The processing of carbon fiber composites has been tailored towards the objective of adding and aligning CNFs, and conventional 2-ply panels were made. An ideal method to disperse CNF in epoxy was developed through the use of mortar and pestle, mechanical stirring, ultrasonication, and de-gassing. Optical Microscopy of in-situ CNF alignment testing gave insight into alignment in actual curing conditions, and samples were completed with alignment at various AC frequencies.

The resulting aligned samples were tested for changes in electrical properties. Overall, the conductivity and dielectric constant can be increased with CNF alignment, and the extent of change can be controlled through the use of AC frequency. The frequencies of 100 Hz and 500 Hz give the greatest increase in conductivity and dielectric constant, while alignment at 1 kHz yields a material of equally high conductivity but a dielectric constant of relatively insulative nature.

Future work will begin by studying the mechanical effects of aligning CNFs in epoxy as well as changes introduced by varying CNF concentration in epoxy and electric field strength. Integrating epoxy with nanofibers into the panel method and inducing CNF alignment is another topic of study. Next steps would include the electrical and mechanical characterization of the new panels, which help in deducing an optimal set of conditions that reach a desired material function.

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